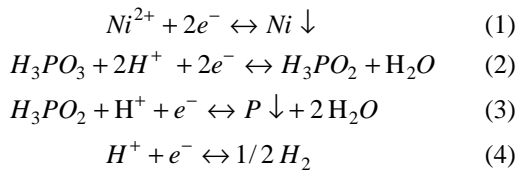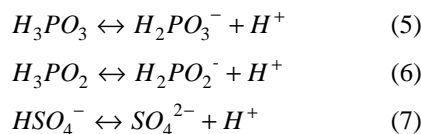# Computer Model Prediction of Electrochemical Ni-P Deposition Thickness and Composition in Phosphorous Electrolytes

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To gain a comprehensive understanding of the Ni-P co-deposition process from phosphorous electrolytes, a plausible reaction mechanism is retained from literature and characterized using a versatile computer model [1] for the simulation of electrochemical processes at a Rotating Disc Electrode (RDE). This model is based on the dilute multi-ion solution theory, to describe ion movement near the electrode, in combination with an adequate description of electrode reaction kinetics.

Basically, two kinds of Ni-P co-deposition mechanisms are proposed in literature. One is the direct mechanism, featuring an independent deposition of Ni and P components [2]:

$$Ni^{2+} + 2e^- \leftrightarrow Ni \downarrow \qquad (1)$$

$$H_3PO_3 + 2H^+ + 2e^- \leftrightarrow H_3PO_2 + H_2O \qquad (2)$$

$$H_3PO_2 + H^+ + e^- \leftrightarrow P \downarrow + 2H_2O \qquad (3)$$

$$H^+ + e^- \leftrightarrow 1/2\, H_2 \qquad (4)$$

Since this mechanism is incapable of explaining the fact that phosphorus cannot be deposited electro-chemically without a major simultaneous metal deposition reaction (= induced co-deposition), an indirect mechanism has been proposed, involving a phosphine reductor species [3]. Despite the ability of this model to explain the induced co-deposition, and the reporting of the phosphine species in some more recent papers [4-5], it is the former (direct) model that was retained for the multi-ion reaction model simulations. Reason is the necessity to decompose the indirect model into more elementary steps (due to the elevated stochiometric coefficient values that appear in the electrode and redox reactions as listed in paper [3]).

The investigated electrolyte contains 0.9 M NiSO₄ + 0.15 M NiCl₂ + 0.5 M H₃PO₃. The phosphorous and phosphorite acid - the latter being produced by reaction (2) - dissociation should be modeled, since these are the main sources for proton production, hence indispensable for the hydrogen evolution reaction (4). In addition, the proton recombination with sulphate ions is to be considered :

$$H_3PO_3 \leftrightarrow H_2PO_3^- + H^+ \qquad (5)$$

$$H_3PO_2 \leftrightarrow H_2PO_2^- + H^+ \qquad (6)$$

$$HSO_4^- \leftrightarrow SO_4^{2-} + H^+ \qquad (7)$$

Reactions (1) to (4) are described by means of Butler-Volmer relations that depend on the reactant electrode surface concentrations.

The Butler-Volmer model parameters are fitted through comparison of simulated results with experimental RDE layer thickness and composition data, while dissociation and recombination rate constants for acid-base reactions (5), (6) and (7) are given a very high value. As a result, those rate constants do not restrict the overall deposition rates. The electrochemical reaction model also accounts for migration effects in the diffusion boundary layer. The latter are of high importance for this type of electrolyte, due to the absence of any important amount of supporting electrolyte.
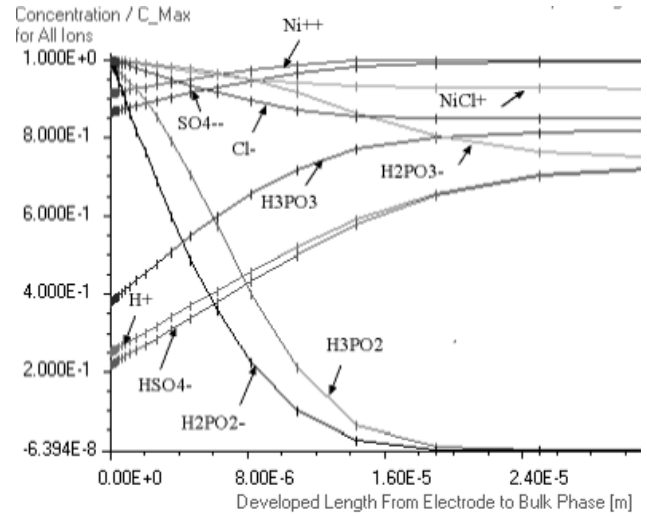
Fig.1: simulated ion conc. profiles (scaled to max. value) on an RDE (950 rpm) for a 0.9 M NiSO₄ + 0.15 M NiCl₂ + 0.5 M H₃PO₃ solution, electrode potential = -1.2 V versus NHE.
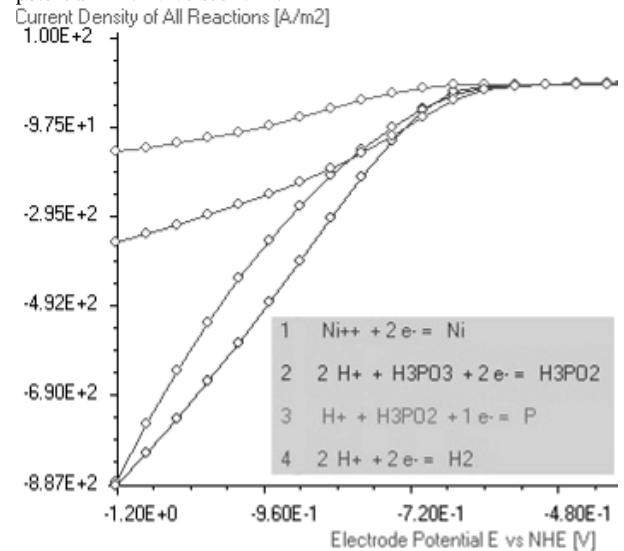
Fig.2: simulated reaction current density profiles on an RDE (950 rpm) for a 0.9 M NiSO₄ + 0.15 M NiCl₂ + 0.5 M H₃PO₃ solution.

References
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